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REVIEW

Diol or Hydrogen Peroxide-responsive Micellar Systems and Their Rheological Properties

Ryotaro Miki*, Tsutomu Yamaki, Masaki Uchida, and Hideshi Natsume

Faculty of Pharmacy and Pharmaceutical Sciences, Josai University, 1-1 Keyakidai, Sakado, Saitama 350-0295, JAPAN

Abstract: External stimuli-responsive worm-like micelles (WLMs) have the potential for a wide range of applications. In particular, sugar (a polyol compound)-responsive WLMs have the potential for use in smart-drug release systems. Phenylboronic acid (PBA) functions as a *cis*-diol sensor in a similar manner it does as a glucose sensor. Thus, WLMs, primarily composed of surfactants and PBA, are expected to function as *cis*-diol-responsive viscoelastic systems. PBA also reacts irreversibly with hydrogen peroxide (H_2O_2) and is converted into phenol and boric acid. H_2O_2 is one of reactive oxygen species crucial for several physiological processes. Therefore, H_2O_2-responsive WLMs have the potential for various applications. In this review, we describe *cis*-diol- and H_2O_2-responsive micellar systems composed of cetyltrimethylammonium bromide and PBA moieties that shift their viscosities in response to stimuli.

Key words: diol compounds, hydrogen peroxide, phenylboronic acid, smart material, worm-like micelles

1 Introduction

Recently, external stimuli-responsive smart materials have attracted considerable attention. Smart hydrogels can be used for drug delivery, cell engineering, and analytical applications[1-3]. Worm-like micelles (WLMs) are primarily composed of surfactants and exhibit unique viscoelastic properties[4, 5]. Compared to spherical micelles, WLMs display a high degree of viscoelasticity due to the entanglement of micelles. Stimuli-responsive WLMs have the potential for a wide range of applications. Various stimuli-responsive WLMs have been reported, with changes induced by light[6-8], redox reactions[9, 10], temperature shifts[11, 12], pH variations[13-15], and CO_2[16]. Diol-responsive WLMs have also been reported as novel stimuli-responsive WLMs[17, 18].

Phenylboronic acid (PBA) and its derivatives have been used as *cis*-diol sensors. PBA reversibly forms cyclic ester bonds with *cis*-diol compounds, such as sugars[19] (Fig. 1a). By utilizing this characteristic, PBA has been investigated as a sensor for glucose (Glc, Fig. 1c) analysis[20], smart insulin delivery[21], and sialic acid-targeting diagnosis/treatment[22]. Therefore, diol-responsive WLMs have potential applications in drug delivery and analytical chemistry. PBA also reacts irreversibly with hydrogen peroxide (H_2O_2) and gets converted into phenol and boric acid (Fig. 1b). H_2O_2 is one of reactive oxygen species crucial for some physiological processes, such as cell signaling, cell proliferation, and apoptosis[23]. H_2O_2-responsive materials have been studied as hydrogels[24, 25] and for fluorescence-imaging analysis[26, 27]. H_2O_2-responsive WLMs also have the potential for various

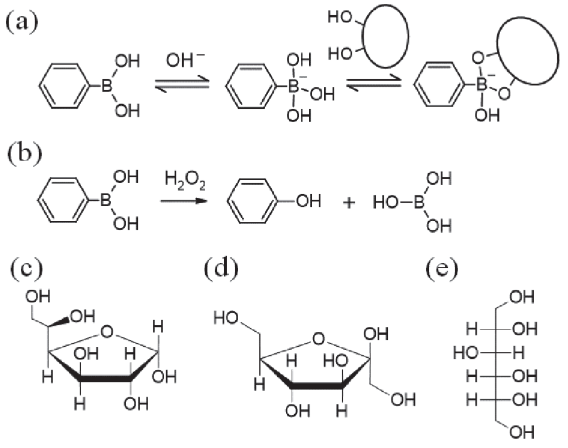

Fig. 1 (a) Acid–base equilibrium of PBA, and formation of cyclic boronate-ester with diol compounds. (b) Schematic of reaction of PBA with H_2O_2. Chemical structures of (c) glucose (shown as α-D-glucofuranose), (d) fructose (shown as β-D-fructofuranose), and (e) sorbitol.

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*Correspondence to: Ryotaro Miki, Faculty of Pharmacy and Pharmaceutical Sciences, Josai University, 1-1 Keyakidai, Sakado, Saitama 350-0295, JAPAN
E-mail: rmiki@josai.ac.jp ORCID ID: https://orcid.org/0000-0002-6972-2189

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applications. In this review, we describe our research on stimuli-responsive micellar systems containing PBA moieties that increase their viscosities upon reaction with *cis*-diol compounds, such as fructose (Fru, Fig. 1d)[28] or H_2O_2[29].

2 Diol-responsive Micellar Systems

Sugar-responsive viscoelastic systems that increase their viscosities upon reaction with *cis*-diol compounds, such as Glc[30-32] or Fru[33], are desirable for applications in drug delivery, analytical chemistry, cell engineering, and medical engineering. The first diol-responsive WLMs reported consisted of the cationic surfactants cetyltrimethylammonium bromide (CTAB) and PBA[17]. These micellar systems exhibit gel-like properties between pH 7.4 and 9.4. Interestingly, the viscosity of the micellar system decreases with Glc addition. The mechanism of WLM formation and the diol-responsive viscosity decrease has been elucidated by ^{1}H nuclear magnetic resonance (NMR), ^{11}B NMR, and ^{19}F NMR using 3-fluorophenylboronic acid (3FPBA) as a substitute for PBA[18]. NMR studies have demonstrated that the driving force behind WLM formation is the cation–π interaction between the quaternary ammonium ion of CTAB and the neutral 3FPBA (Fig. 2a). In addition to the cation–π interaction, the hydrophobic interaction between the alkyl chain of CTAB and the benzene ring of the PBA moiety may also affect micellar transitions. A previous ^{1}H NMR study showed that the change in the chemical shift of the methyl group adjacent to the quaternary ammonium of CTAB with an increasing concentration of coexisting PBA was larger than that of the terminal methyl group of the alkyl chain of CTAB[17]. This suggests that the effect of the hydrophobic interaction between the alkyl chain of CTAB and the benzene ring of the PBA moiety is smaller than that of the cation–π interaction. The mechanism of the diol-responsive deformation of WLMs is as follows. Upon the addition of a *cis*-diol compound, 3FPBA is converted from a neutral to an anionic form (Fig. 2b). The interaction of ionized 3FPBA-ester with CTAB is weaker than that of the neutral 3FPBA. When PBA forms an ester bond with a *cis*-diol compound, such as Glc, the PBA-diol ester becomes more hydrophilic. This might further reduce the influence of hydrophobic interactions between the alkyl chains of CTAB and the benzene ring of the PBA moiety. In addition to the hydrophobic interactions, the electrostatic interactions between the boronate anion and the quaternary ammonium part of CTAB might also exist. However, in this case, the impact of the electrostatic interactions on the micellar transition would be relatively small compared to the cation–π interaction. This change implies that the number of structural components in the WLM decrease, thereby disrupting the WLMs.

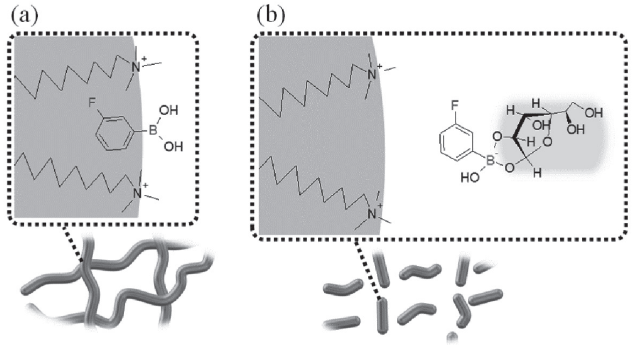

Fig. 2 Schematic of proposed mechanism of formation of WLMs (a), and deformation of WLMs by adding Glc (b). Reprinted with permission from Ref. 18. Copyright 2021 American Chemical Society.

In contrast, we have reported a novel *cis*-diol-responsive micellar system that increases viscosity upon the addition of *cis*-diol compounds[28]. This innovation was inspired by two previous findings: (1) CTAB forms typical WLMs upon the addition of sodium salicylate (NaSal)[4, 5], and (2) boric acid forms cyclic ester bonds with salicylic acid[34]. It was expected that the addition of the PBA moiety to a typical CTAB/NaSal WLM system would induce a viscosity change. The micellar systems were prepared as follows: System A (pH 7.5) was prepared with 100 mM CTAB/70 mM NaSal/100 mM phosphate, and System B was comprised of System A with 20 mM 3FPBA (Fig. 3). When the microtubes were inverted, System A did not flow down the tube, whereas System B flowed rapidly. To study the effect of *cis*-diol compounds, System B was prepared using Fru, sorbitol (Sor, Fig. 1e), and Glc. The sample with 1.12 M Fru or 1.12 M Sor flowed down the tube more slowly compared to System B. The sample with 1.12 M Glc flowed as rapidly as System B.

The rheological characteristics were analyzed by evaluating the relationship between shear rate ($\dot{\gamma}$) and viscosity (η) (Fig. 4a). For System A, η remained constant at a low $\dot{\gamma}$ and started to decrease once $\dot{\gamma}$ reached a specific threshold level. This rheological feature is typically observed in WLMs[35, 36]. The dependence of η on $\dot{\gamma}$ in System B with 1.12 M Fru or 1.12 M Sor was similar to that of System A. The

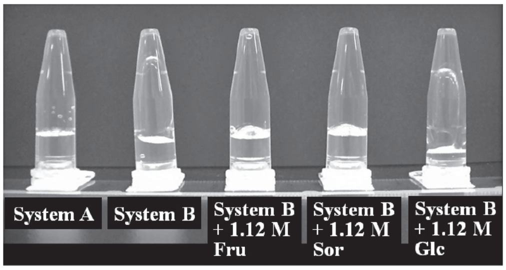

Fig. 3 Visual appearance of System A, System B, and System B with different diols. Reproduced from Ref. 28 under terms of the CC-BY license.

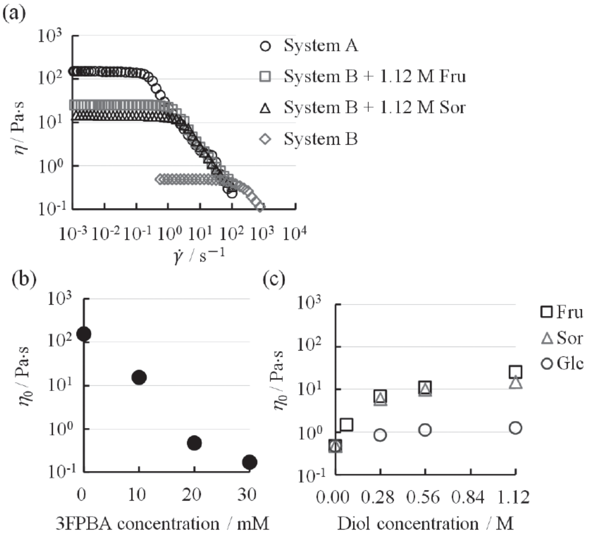

Fig. 4 (a) Steady shear rate ($\dot{\gamma}$)-dependent changes in viscosity (η) in System A, System B, and System B with diols. (b) Relationship between η_0 and 3FPBA concentration in System A. (c) Relationship between η_0 and diol concentration in System B. Reproduced from Ref. 28 under terms of the CC-BY license.

zero-shear viscosity (η_0) was obtained by extrapolating the constant η at low $\dot{\gamma}$ to the y-axis. In System A, η_0 decreased from 156 Pa·s (without 3FPBA) to 0.17 Pa·s (with 30 mM 3FPBA) with increasing 3FPBA concentration (Fig. 4b). This represents a 1/900 shift in η_0 compared to that without 3FPBA, demonstrating that 3FPBA effectively decreased η in System A. In contrast, in System B with the *cis*-diol compounds, η_0 increased with increasing concentration of the *cis*-diol compounds (Fig. 4c). η_0 increased 50-fold with 1.12 M Fru, 30-fold with 1.12 M Sor, and only 2-fold with 1.12 M Glc. Fru and Sor were more effective than Glc in increasing η for System B.

Dynamic viscoelasticity was evaluated to further study the rheological features. Dynamic viscoelasticity measurements can be used to evaluate changes in both the storage modulus (G') and loss modulus (G'') depending on the frequency (ω). These two variables are based on Maxwell model[37], as shown in Eqs. (1) and (2), respectively,

$$G' = \frac{\omega^2\tau^2}{1+\omega^2\tau^2}\cdot G_0 \tag{1}$$

$$G'' = \frac{\omega\tau}{1+\omega^2\tau^2}\cdot G_0 \tag{2}$$

where G_0 and τ are the plateau modulus and relaxation time, respectively. In the analysis of the rheological behavior using the Maxwell model with a single τ, G' and G'' exhibited a semicircular curve in the Cole–Cole plot (G' vs. G'') (see Eq. (3))[4, 38].

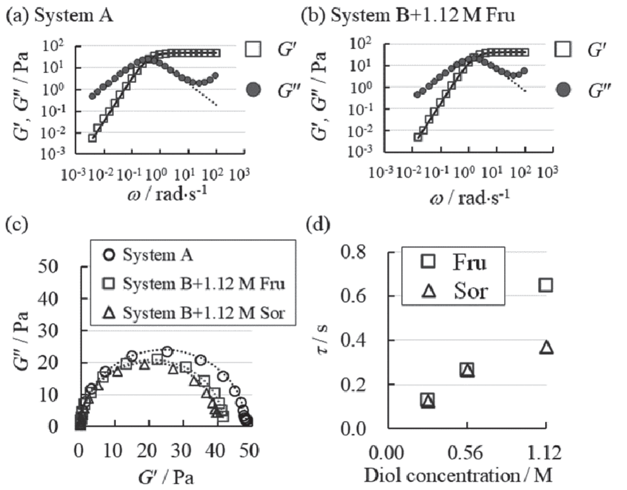

Fig. 5 Relationships between storage modulus (G') and loss modulus (G'') in (a) System A, (b) System B with 1.12 M Fru. The solid and dotted curve-fittings were calculated according to Eq. 1 and 2, respectively. (c) Cole-Cole plots for System A and System B with fructose (Fru) or sorbitol (Sor). The dotted lines represent the fitting curves obtained using Eq. (3). (d) Changes in relaxation time (τ) in System B with Fru or Sor. Reproduced from Ref. 28 under terms of the CC-BY license.

$$\left(G' - \frac{G_0}{2}\right)^2 + G''^2 = \frac{G_0^{\,2}}{4} \tag{3}$$

Figures 5a and 5b show the frequency-dependent behaviors of G' and G''. G' is lower than G'' at low ω, whereas G' is higher at high ω in System A and System B with 1.12 M Fru. This implies that the sample behaves as a liquid at low ω and as a gel at high ω. Cole–Cole plots were used to study the presence of WLMs, where the semicircular profile is a rheological feature of typical WLMs[4]. Semicircular curves were obtained for System A and System B with 1.12 M Fru or 1.12 M Sor (Fig. 5c). Therefore, it was assumed that these micellar systems formed long WLMs. The τ is one of the indexes of entanglement of WLMs[35, 39]. For instance, a high τ indicates the formation of highly entangled WLMs[35, 39]. The intersection of G' and G'' is defined as ω_c, and τ is calculated as the inverse of ω_c. τ increased with increasing concentrations of Fru or Sor in System B (Fig. 5d). This demonstrated that the addition of Fru or Sor lengthened the WLMs in System B.

The binding constants (K) between 3FPBA and the diol compounds have been determined using the fluorescence method with alizarin red S (ARS)[19, 40, 41] (Table 1). The K value of Glc (1.65 M^{-1}) is significantly lower than those of Fru (188 M^{-1}) and Sor (341 M^{-1}). The order of K between 3FPBA and the diol compounds is similar to that of PBA[19]. The increase in η_0 in System B almost reflects K. The increasing effect of η_0 follows the order of Sor>Fru>Glc. In

Table 1 Binding constants (K) between 3FPBA and diol compounds at pH 7.4 in 100 mM phosphate buffer. Reproduced from Ref. 28 under terms of the CC-BY license.

Diol	Binding constant K (M^{-1})
ARS	1223
Sor	341
Fru	188
NaSal	166
Glc	1.65

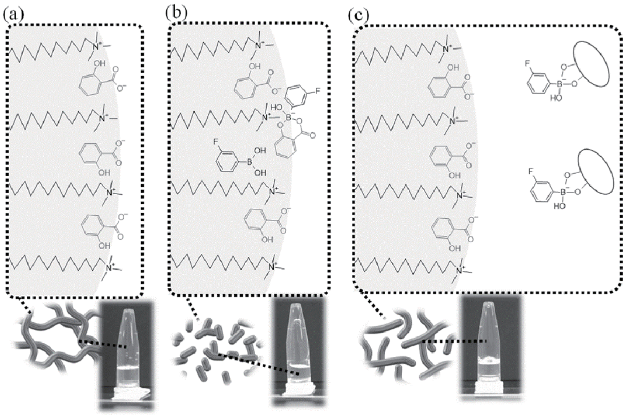

Fig. 6 Proposed mechanisms of micellar transition in (a) System A, (b) System B, and (c) System B with diol compounds. Reproduced from Ref. 28 under terms of the CC-BY license.

System A, 3FPBA reversibly binds to NaSal, and this complex formation leads to a decrease in viscosity upon the addition of 3FPBA. In System B, in addition to diol compounds such as Fru, 3FPBA also reversibly binds to diol compounds (Fru, Sor, or Glc). The viscosity increase in System B upon the addition of the diol compounds likely results from the competitive formation of a cyclic ester bond between 3FPBA and the diol compounds.

The mechanisms of structural transition in the micellar system are discussed below. In System A, cetyltrimethylammonium (CTA$^+$) interacts with the salicylate anion (Sal$^-$)[4, 5], which weakens the electrostatic repulsion among the cationic parts of CTA$^+$ (Fig. 6a). This leads to a tighter packing of CTA$^+$ and consequently, the formation of WLMs. The ionized 3FPBA does not strongly interact with CTA$^+$ in the CTAB/3FPBA micellar system[18] (Fig. 2b). Unexpectedly, 3FPBA/Sal-ester is proposed to interact with CTAB in System B based on the results of an NMR study[28]. The effect of the interaction of 3FPBA/Sal-ester with CTA$^+$ on the packing state is likely different from that of free 3FPBA or Sal$^-$ (Fig. 6b). As a result, the WLMs were shortened, and the viscosity of System B decreased. When *cis*-diol compounds (Fru, Sor, or Glc) were added to System B, 3FPBA bound to Sal$^-$ competitively combined with the *cis*-diol compounds. This decreased the amount of 3FPBA/Sal-ester interacting with CTA$^+$ and increased the amount of free Sal$^-$ (Fig. 6c). The newly formed 3FPBA/Fru or Sor-ester did not strongly interact with CTA$^+$, and free Sal$^-$ interacted with CTA$^+$. This lengthened the WLMs and increased the viscosity of System B containing Fru, Sor, or Glc.

3 Hydrogen Peroxide-responsive Micellar Systems

The addition of aromatic compounds to CTAB-based spherical micelles is a typical method of forming WLMs[42]. The addition of phenolic compounds to a spherical micelle solution containing CTAB induces its transformation into WLMs[43-45]. As mentioned in the Introduction, PBA reacts not only with diol compounds but also with H_2O_2 (Fig. 1b).

The addition of H_2O_2 to the CTAB/PBA micellar system converts PBA into phenol. However, it cannot induce drastic micellar transitions because of the chemical and physicochemical similarities between PBA and phenol. Adding Fru to CTAB/PBA WLMs effectively decreases the viscosity[18]. This phenomenon inspired us to conclude that the CTAB/PBA-Fru micellar system may exhibit a potential increase in viscosity in response to H_2O_2. Namely, two types of reactions on PBA are possible: (i) PBA can bind with Fru reversibly to form a cyclic ester, and (ii) PBA can react with H_2O_2 to convert phenol. 3FPBA and 3-fluorophenol (3FPhOH) were used as model compounds for PBA and phenol, respectively.

System BA and System Fr are defined as the 0.1 M CTAB/50 mM 3FPBA system and 0.1 M CTAB/50 mM 3FPBA/0.2 M Fru system, respectively. Phosphate buffer (pH 7.4, 0.6 M) was used as the solvent. The system of 0.1 M CTAB/45 mM 3FPhOH, System BA, and System Fr with 40 mM H_2O_2 behaved in a gel-like manner; these samples did not rapidly flow when inverted in glass vials (Fig. 7). In comparison, System Fr behaved as a sol and rapidly flowed down when inverted.

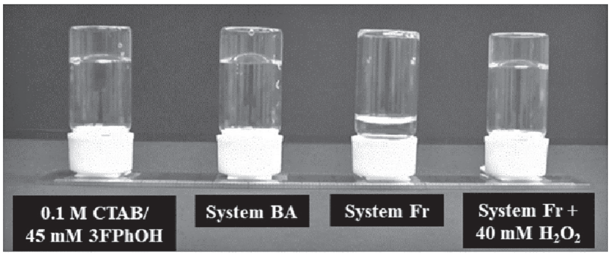

Fig. 7 Photographs of 0.1 M CTAB/45 mM 3FPhOH, System BA, System Fr, and System Fr with 40 mM H_2O_2. Reproduced from Ref. 29 with permission from Elsevier.

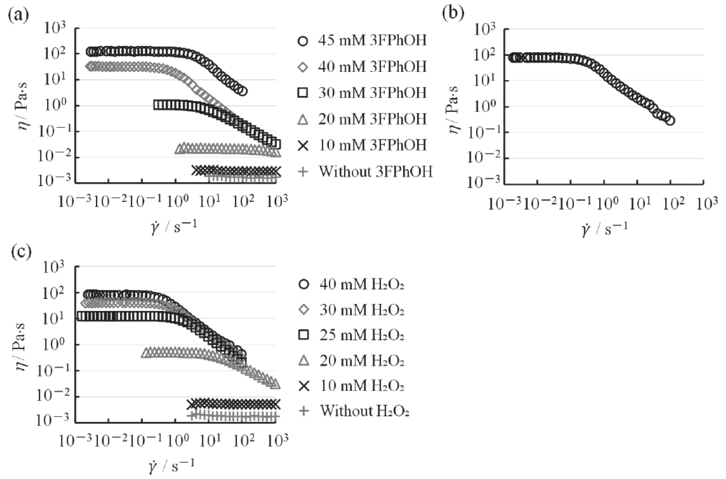

Fig. 8 Dependence of viscosity (η) on steady shear rate ($\dot{\gamma}$) in (a) 0.1 M CTAB/3FPhOH system, (b) System BA, and (c) System Fr with H_2O_2. Reproduced from Ref. 29 with permission from Elsevier.

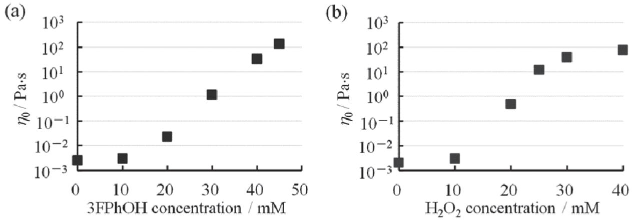

Fig. 9 (a) Relationship between η_0 and 3FPhOH concentration in 0.1 M CTAB/3FPhOH system, (b) relationship between η_0 and H_2O_2 concentration in System Fr with H_2O_2. Reproduced from Ref. 29 with permission from Elsevier.

In this section, the viscosity characteristics of the proposed system are described. Consistently higher η values (132.1, 80.0, and 77.8 Pa·s) were obtained for the system of 0.1 M CTAB/45 mM 3FPhOH, System BA, and for System Fr with 40 mM H_2O_2, respectively, at lower $\dot{\gamma}$ values (Fig. 8). The η values remained constant at a low $\dot{\gamma}$ but began decreasing past a certain point of $\dot{\gamma}$. These rheological characteristics have also been observed in typical WLMs[35, 36]. These rheological behaviors indicate that the structure recovers rapidly when a low shear is applied to the sample. For System BA and System Fr without H_2O_2, the η_0 values are 80.0 Pa·s and 2.0 mPa·s, respectively (Fig. 8b, 8c). Thus, for System BA, η_0 decreased drastically to 1/40,000 upon adding 0.2 M Fru. This is in line with the previous report stating that Fru is effective at decreasing the η_0 of the CTAB/3FPBA micellar system[18]. The η_0 increased with increasing 3FPhOH concentration in the 0.1 M CTAB/3FPhOH system (Fig. 9a). With 45 mM 3FPhOH, the system showed a 5×10^4-fold increase in η_0 from 2.5 mPa·s to 132.1 Pa·s. Similarly, η_0 increased with increasing H_2O_2 concentration in System Fr, where 40 mM H_2O_2 induced a 4×10^4-fold increase in η_0 from 2.0 mPa·s to 77.8 Pa·s (Fig. 9b).

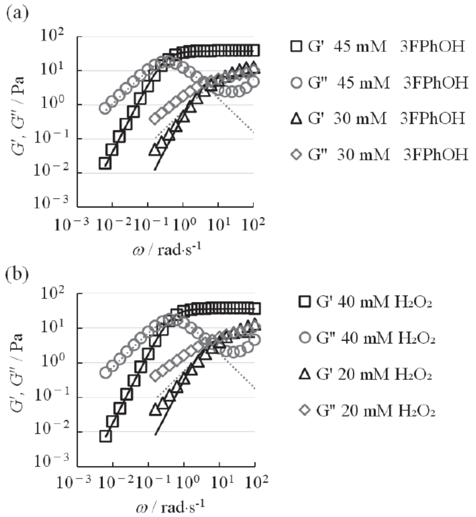

Fig. 10 Relationship between frequency and G' or G'' in (a) 0.1 M CTAB/3FPhOH system and (b) System Fr with H_2O_2. The solid and dotted lines represent the curve-fittings according to Eqs. 1 and 2, respectively. The symbols in these figures are slightly modified from Ref. 29 with permission from Elsevier.

This section describes the dynamic viscoelastic properties of the systems. G' was less than G'' at a low ω; however, G' was higher at a high ω, and G' fitted well to the Maxwell model in both the 0.1 M CTAB/45 mM 3FPhOH system and System Fr with 40 mM H_2O_2 (Fig. 10). In contrast, in the system containing 0.1 M CTAB/30 mM 3FPhOH and in System Fr with 20 mM H_2O_2, G' was less than G'' at a low ω, although G' was slightly higher at high ω (Fig. 10). Cole–Cole plots were used to confirm the formation of WLMs. For the 0.1 M CTAB/30 mM 3FPhOH system, a semicircle was not obtained (Fig. 11a). However, a perfect semicircular structure was observed for the 0.1 M CTAB/45

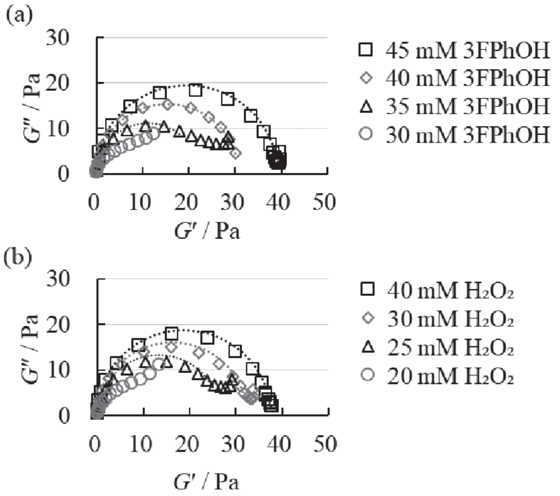

Fig. 11 Cole-Cole plot for (a) 0.1 M CTAB/3FPhOH system and (b) System Fr with H_2O_2. The dotted lines represent the curve-fittings from Eq. 3. Reproduced from Ref. 29 with permission from Elsevier.

mM 3FPhOH system. No semicircle was observed for the System Fr with 20 mM H_2O_2 (Fig. 11b). In contrast, an almost perfect semicircle was obtained for System Fr with 40 mM H_2O_2. Therefore, WLMs were formed in both the 0.1 M CTAB/45 mM 3FPhOH system and System Fr with 40 mM H_2O_2.

The presumed mechanisms of the micellar transition are shown in Fig. 12. The pK_a of 3FPhOH is 9.39[29]. Thus, neutral 3FPhOH is dominant compared to the ionized form at pH 7.4 in the 0.1 M CTAB/45 mM 3FPhOH system. In general, aromatic compounds, including phenolic compounds, interact with CTAB via cation–π interactions[18, 46-50]. Thus, 3FPhOH also interacts with CTAB in the 0.1 M CTAB/45 mM 3FPhOH system (Fig. 12a). As shown in Fig. 6a, the cation–π interaction between CTAB and the aromatic rings weakens the electrostatic repulsion between the cationic parts of CTAB. Thus, the CTAB packing becomes tighter, which induces a micellar transition from spherical to worm-like structures[10, 51, 52]. In addition, 3FPBA reversibly bonded to Fru in System Fr. The 3FPBA-Fru ester did not strongly interact with CTAB[18] (Fig. 12b). Thus, the cationic groups of CTAB repelled each other more strongly than those in the CTAB/3FPhOH system. This led to a change in the packing state of CTAB and the transformation from WLMs to spherical micelles. When H_2O_2 was added to System Fr, the 3FPBA-Fru ester converted to 3FPhOH and the borate ester in System Fr (Fig. 12c). Owing to this change, the amount of 3FPhOH increased, and the repulsive force of the cationic parts of CTAB became weaker. This tightened the packing state of CTAB and induced the transformation from spherical micelles to WLMs.

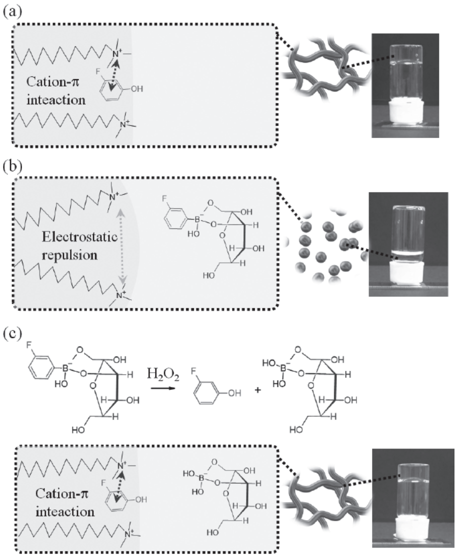

Fig. 12 Proposed mechanisms of micellar transition in (a) 0.1 M CTAB/45 mM 3FPhOH system, (b) System Fr, and (c) System Fr with H_2O_2. Reproduced from Ref. 29 with permission from Elsevier.

4 Conclusion

This review presents two primitive types of stimuli-responsive micellar systems, whose viscosities increase upon the addition of *cis*-diol compounds or H_2O_2. The changes in viscoelasticity are attributed to micellar transitions, with PBA or PBA derivatives being utilized in these systems as a *cis*-diol or as a H_2O_2 sensor. Rapid and reversible PBA ester formation/disassociation is desirable in smart micellar systems. In the CTAB/NaSal/3FPBA system, the increase in viscosity with the addition of *cis*-diol compounds results from competitive cyclic ester bonding between 3FPBA and the diol compounds.

Phenol moieties are used in a variety of chemical products, such as medicines, disinfectants, dyes, and plastics. Thus, the reaction that generates phenolic compounds in addition to H_2O_2 in PBA derivative/Fru-ester micellar systems has the potential for wide applications. Cation–π interactions between the cationic parts of CTAB and the benzene rings of the aromatic compounds are important for the formation of WLMs in these systems.

Despite the promising properties of these systems, there are several future challenges for their use in pharmaceutical and biological applications, such as in drug delivery systems and cell engineering. For example, a significant improvement in the Glc responsiveness is required for diol-responsive micellar systems. Additionally, the use of biocompatible components, such as lecithin or cholic acid, is expected to replace CTAB in stimuli-responsive micellar systems, as CTAB is not a biocompatible surfactant. Therefore, further studies on stimuli-responsive micellar systems containing PBA moieties are required.

References

1） Vázquez-González, M.; Willner, I. Stimuli-responsive biomolecule-based hydrogels and their applications. *Angew. Chemie Int. Ed.* **59**, 15342-15377（2020）.

2） Zhang, K.; Feng, Q.; Fang, Z.; Gu, L.; Bian, L. Structurally dynamic hydrogels for biomedical applications: pursuing a fine balance between macroscopic stability and microscopic dynamics. *Chem. Rev.* **121**, 11149-11193（2021）.

3） Du, X.; Zhou, J.; Shi, J.; Xu, B. Supramolecular hydrogelators and hydrogels: from soft matter to molecular biomaterials. *Chem. Rev.* **115**, 13165-13307（2015）.

4） Shikata, T.; Hirata, H.; Kotaka, T. Micelle formation of detergent molecules in aqueous media: Viscoelastic properties of aqueous cetyltrimethylammonium bromide solutions. *Langmuir* **3**, 1081-1086（1987）.

5） Shikata, T.; Hirata, H.; Kotaka, T. Micelle formation of detergent molecules in aqueous media. 2. role of free salicylate ions on viscoelastic properties of aqueous cetyltrimethylammonium bromide-sodium salicylate solutions. *Langmuir* **4**, 354-359（1988）.

6） Sakai, H.; Orihara, Y.; Kodashima, H.; Matsumura, A.; Ohkubo, T. *et al.* Photoinduced reversible change of fluid viscosity. *J. Am. Chem. Soc.* **127**, 13454-13455（2005）.

7） Ketner, A.M.; Kumar, R.; Davies, T.S.; Elder, P.W.; Raghavan, S.R. A simple class of photorheological fluids: Surfactant solutions with viscosity tunable by light. *J. Am. Chem. Soc.* **129**, 1553-1559（2007）.

8） Akamatsu, M.; Shiina, M.; Shrestha, R.G.; Sakai, K.; Abe, M. *et al.* Photoinduced viscosity control of lecithin-based reverse wormlike micellar systems using azobenzene derivatives. *RSC Adv.* **8**, 23742-23747（2018）.

9） Tsuchiya, K.; Orihara, Y.; Kondo, Y.; Yoshino, N.; Ohkubo, T. *et al.* Control of viscoelasticity using redox reaction. *J. Am. Chem. Soc.* **126**, 12282-12283（2004）.

10） Sugai, J.; Saito, N.; Takahashi, Y.; Kondo, Y. Synthesis and viscoelastic properties of gemini surfactants containing redox-active ferrocenyl groups. *Colloids Surf. A Physicochem. Eng. Asp.* **572**, 197-202（2019）.

11） Davies, T.S.; Ketner, A.M.; Raghavan, S.R. Self-assembly of surfactant vesicles that transform into viscoelastic wormlike micelles upon heating. *J. Am. Chem. Soc.* **128**, 6669-6675（2006）.

12） Lin, Y.; Qiao, Y.; Yan, Y.; Huang, J. Thermo-responsive viscoelastic wormlike micelle to elastic hydrogel transition in dual-component systems. *Soft Matter* **5**, 3047-3053（2009）.

13） Lin, Y.; Han, X.; Huang, J.; Fu, H.; Yu, C. A facile route to design pH-responsive viscoelastic wormlike micelles: Smart use of hydrotropes. *J. Colloid Interface Sci.* **330**, 449-455（2009）.

14） Feng, Y.; Chu, Z. pH-tunable wormlike micelles based on an ultra-long-chain "pseudo" gemini surfactant. *Soft Matter* **11**, 4614-4620（2015）.

15） Liu, P.; Pei, X.; Li, C.; Li, R.; Chen, Z. *et al.* pH-switchable wormlike micelles with high viscoelasticity formed by pseudo-oligomeric surfactants. *J. Mol. Liq.* **334**, 116499（2021）.

16） Su, X.; Cunningham, M.F.; Jessop, P.G. Switchable viscosity triggered by CO_2 using smart worm-like micelles. *Chem. Commun.* **49**, 2655-2657（2013）.

17） Miki, R.; Takei, C.; Ohtani, Y.; Kawashima, K.; Yoshida, A. *et al.* Glucose responsive rheological change and drug release from a novel worm-like micelle gel formed in cetyltrimethylammonium bromide/phenylboronic acid/water system. *Mol. Pharm.* **15**, 1097-1104（2018）.

18） Miki, R.; Yamauchi, T.; Kawashima, K.; Egawa, Y.; Seki, T. Multinuclear NMR study on the formation and polyol-induced deformation mechanisms of wormlike micelles composed of cetyltrimethylammonium bromide and 3-fluorophenylboronic acid. *Langmuir* **37**, 3438-3445（2021）.

19） Springsteen, G.; Wang, B. A detailed examination of boronic acid–diol complexation. *Tetrahedron* **58**, 5291-5300（2002）.

20） Sun, X.; James, T.D. Glucose sensing in supramolecular chemistry. *Chem. Rev.* **115**, 8001-8037（2015）.

21） Wang, J.; Wang, Z.; Yu, J.; Kahkoska, A.R.; Buse, J.B. *et al.* Glucose-responsive insulin and delivery systems: innovation and translation. *Adv. Mater.* **32**, 1902004（2020）.

22） Sanjoh, M.; Miyahara, Y.; Kataoka, K.; Matsumoto, A. Phenylboronic acids-based diagnostic and therapeutic applications. *Anal. Sci.* **30**, 111-117（2014）.

23） Martindale, J.L.; Holbrook, N.J. Cellular response to oxidative stress: Signaling for suicide and survival. *J. Cell. Physiol.* **192**, 1-15（2002）.

24） Ikeda, M.; Tanida, T.; Yoshii, T.; Hamachi, I. Rational molecular design of stimulus-responsive supramolecular hydrogels based on dipeptides. *Adv. Mater.* **23**, 2819-2822（2011）.

25） Ikeda, M.; Tanida, T.; Yoshii, T.; Kurotani, K.; Onogi, S. *et al.* Installing logic-gate responses to a variety of biological substances in supramolecular hydrogel-enzyme hybrids. *Nat. Chem.* **6**, 511-518（2014）.

26） Lippert, A.R.; Bittner, G.C. Van de; Chang, C.J. Boronate oxidation as a bioorthogonal reaction approach for studying the chemistry of hydrogen peroxide in living systems. *Acc. Chem. Res.* **44**, 793-804（2011）.

27） Wu, L.; Sedgwick, A.C.; Sun, X.; Bull, S.D.; He, X.P. *et al.* Reaction-based fluorescent probes for the detection and imaging of reactive oxygen, nitrogen, and sulfur species. *Acc. Chem. Res.* **52**, 2582-2597（2019）.

28） Miki, R.; Yamaki, T.; Uchida, M.; Natsume, H. Diol responsive viscosity increase in a cetyltrimethylammonium bromide/sodium salicylate/3-fluorophenylboronic acid micelle system. *RSC Adv.* **12**, 6668-6675（2022）.

29）Miki, R.; Yamaki, T.; Uchida, M.; Natsume, H. Hydrogen peroxide-responsive micellar transition from spherical to worm-like in cetyltrimethylammonium bromide/3-fluorophenylboronic acid/fructose system. *Colloids Surf. A Physicochem. Eng. Asp.* **648**, 129418（2022）.

30）Holz, E.; Rajagopal, K. *In situ*-forming glucose-responsive hydrogel from hyaluronic acid modified with a boronic acid derivative. *Macromol. Chem. Phys.* **221**, 2000055（2020）.

31）Gantumur, E.; Sakai, S.; Nakahata, M.; Taya, M. Cytocompatible enzymatic hydrogelation mediated by glucose and cysteine residues. *ACS Macro Lett.* **6**, 485-488（2017）.

32）Sakai, S.; Komatani, K.; Taya, M. Glucose-triggered co-enzymatic hydrogelation of aqueous polymer solutions. *RSC Adv.* **2**, 1502-1507（2012）.

33）Grigoriou, S.; Johnson, E.K.; Chen, L.; Adams, D.J.; James, T.D. *et al.* Dipeptide hydrogel formation triggered by boronic acid-sugar recognition. *Soft Matter* **8**, 6788-6791（2012）.

34）Miyazaki, Y.; Matsuo, H.; Fujimori, T.; Takemura, H.; Matsuoka, S. *et al.* Interaction of boric acid with salicyl derivatives as an anchor group of boron-selective adsorbents. *Polyhedron* **27**, 2785-2790（2008）.

35）Shrestha, R.G.; Shrestha, L.K.; Aramaki, K. Formation of wormlike micelle in a mixed amino-acid based anionic surfactant and cationic surfactant systems. *J. Colloid Interface Sci.* **311**, 276-284（2007）.

36）Varade, D.; Sharma, S.C.; Aramaki, K. Viscoelastic behavior of surfactants worm-like micellar solution in the presence of alkanolamide. *J. Colloid Interface Sci.* **313**, 680-685（2007）.

37）Dreiss, C.A. Wormlike micelles: Where do we stand? recent developments, linear rheology and scattering techniques. *Soft Matter* **3**, 956-970（2007）.

38）Khatory, A.; Lequeux, F.; Kern, F.; Candau, S.J. Linear and nonlinear viscoelasticity of semidilute solutions of wormlike micelles at high salt content. *Langmuir* **9**, 1456-1464（1993）.

39）Hashizaki, K.; Taguchi, H.; Saito, Y. A novel reverse worm-like micelle from a lecithin/sucrose fatty acid ester/oil system. *Colloid Polym. Sci.* **287**, 1099-1105（2009）.

40）Springsteen, G.; Wang, B.; Alizarin Red, S. as a general optical reporter for studying the binding of boronic acids with carbohydrates. *Chem. Commun.* **1**, 1608-1609（2001）.

41）Brooks, W.L.A.; Deng, C.C.; Sumerlin, B.S. Structure-reactivity relationships in boronic acid-diol complexation. *ACS Omega* **3**, 17863-17870（2018）.

42）Chu, Z.; Dreiss, C.A.; Feng, Y. Smart wormlike micelles. *Chem. Soc. Rev.* **42**, 7174-7203（2013）.

43）Varade, D.; Rodríguez-Abreu, C.; Delgado, J.G.; Aramaki, K. Viscoelasticity and mass transfer in phenol–ctab aqueous systems. *Colloid Polym. Sci.* **285**, 1741-1747（2007）.

44）Singh, M.; Ford, C.; Agarwal, V.; Fritz, G.; Bose, A. *et al.* Structural evolution in cationic micelles upon incorporation of a polar organic dopant. *Langmuir* **20**, 9931-9937（2004）.

45）Agarwal, V.; Singh, M.; McPherson, G.; John, V.; Bose, A. Microstructure evolution in aqueous solutions of cetyl trimethylammonium bromide（CTAB）and phenol derivatives. *Colloids Surf. A Physicochem. Eng. Asp.* **281**, 246-253（2006）.

46）Wei, X.L.; Ping, A.L.; Du, P.P.; Liu, J.; Sun, D.Z. *et al.* Formation and properties of wormlike micelles in solutions of a cationic surfactant with a 2-hydroxypropoxy insertion group. *Soft Matter* **9**, 8454-8463（2013）.

47）Kumar, S.; Sharma, D.; Kabir, D. Role of partitioning site in producing viscoelasticity in micellar solutions. *J. Surfact. Deterg.* **8**, 247-252（2005）.

48）Sabatino, P.; Szczygiel, A.; Sinnaeve, D.; Hakimhashemi, M.; Saveyn, H. *et al.* NMR study of the influence of pH on phenol sorption in cationic CTAB micellar solutions. *Colloids Surf. A Physicochem. Eng. Asp.* **370**, 42-48（2010）.

49）Mata, J.P.; Aswal, V.K.; Hassan, P.A.; Bahadur, P. A phenol-induced structural transition in aqueous cetyltrimethylammonium bromide solution. *J. Colloid Interface Sci.* **299**, 910-915（2006）.

50）Chaghi, R.; de Ménorval, L.C.; Charnay, C.; Derrien, G.; Zajac, J. Interactions of phenol with cationic micelles of hexadecyltrimethylammonium bromide studied by titration calorimetry, conductimetry, and ^{1}H NMR in the range of low additive and surfactant concentrations. *J. Colloid Interface Sci.* **326**, 227-234（2008）.

51）Tu, Y.; Chen, Q.; Shang, Y.; Teng, H.; Liu, H. Photoresponsive behavior of wormlike micelles constructed by gemini surfactant 12-3-12·2Br$^-$ and different cinnamate derivatives. *Langmuir* **35**, 4634-4645（2019）.

52）Li, J.; Zhao, M.; Zhou, H.; Gao, H.; Zheng, L. Photo-induced transformation of wormlike micelles to spherical micelles in aqueous solution. *Soft Matter* **8**, 7858-7864（2012）.